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(54) METHACRYLIC RESIN COMPOSITION CAPABLE OF ABSORBING NEAR INFRARED RAY AND ITS MOLDING

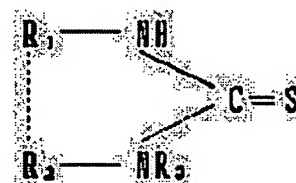
(57)Abstract:

PURPOSE: To provide a methacrylic resin composition capable of absorbing near infrared ray and its molding having strong absorption over the whole area of near infrared radiation, slight color and excellent durability and suitable as an optical material such as filter for cutting near infrared ray, etc.

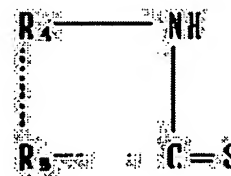
CONSTITUTION: The objective composition is produced by compounding (A) 100 pts.wt. of a methacrylic resin with (B) 0.05-5 pts.wt. (preferably 0.05-2.5 pts.wt.) of one or more kinds of copper compounds selected from the copper compound of formula I (R is H, alkyl, cycloalkyl, etc.; X is COO, SO₄, etc.; (n) is 1-4) (e.g. copper stearate), chlorophyll copper, copper chlorophyllin sodium, etc., and (C) 0.05-50 pts.wt. (preferably 0.05-1-pts.wt.) of one or more compounds selected from thiourea derivative of formula II (R₁ to R₃ are H, alkyl, etc.) (e.g. 1-ethyl-3-phenylthiourea) and thioamide derivative of formula III (R₄ and R₅ are H, alkyl, etc.) (e.g. N-methylthiobenzamide). The obtained composition is formed in the form of a sheet or a film.



I



II



III

LEGAL STATUS

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CLAIMS

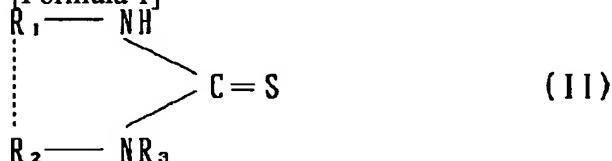
[Claim(s)]

[Claim 1] (A) Methacrylic system resin It is (B) to the 100 weight sections. The following general formula (I)

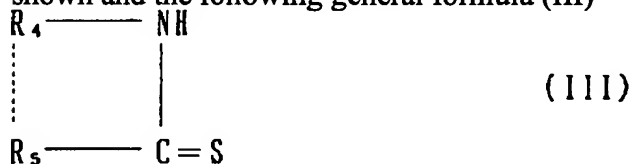
(R-X)_nCu (I)

The inside of [type and R Hydrogen, an alkyl group, a cycloalkyl radical, an aryl group, The monad chosen from the group which consists of an aralkyl radical and heterocycle residue (each radical may have one or more substituents), The copper compound by which -COO, -SO₄, -SO₃, -PO₄, -O, and n are expressed with integer] of 1-4 for X, At least a kind of copper compound 0.05 chosen from chlorophyll copper, sodium copper-chlorophyllin, and bisacetylacetonate copper - 5 weight sections, and (C) The following general formula (II)

[Formula 1]



(R₁, R₂, and R₃ may express the monad chosen from the group which consists of the heterocycle residue of hydrogen, an alkyl group, a cycloalkyl radical, an aryl group, an aralkyl radical and 5 members, or 6 members, each radical may have one or more substituents, R₁, R₂, or R₂ and R₃ may connect, and they may form a ring) the thiourea derivative shown and the following general formula (III) -- [Formula 2]



R₄ and R₅ -- hydrogen, an alkyl group, an alkenyl radical, and a cycloalkyl radical -- The monad chosen from the group which consists of the heterocycle residue of an aryl group, an aralkyl radical and 5 members, or 6 members is expressed. R₅ may also express an alkoxy group further and each radical may have one or more substituents. R₄ and R₅ may connect and they may form a ring. Near infrared ray absorption methacrylic system resin constituent characterized by the thing which is chosen from the thioamide derivative shown, and which contain at least one sort of 0.05 - 50 weight sections, and changes.

[Claim 2] The near infrared ray absorption methacrylic system resin Plastic solid which a near infrared ray absorption methacrylic system resin constituent according to claim 1 is fabricated a sheet or in the shape of a film, and changes.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention penetrates a visible ray comparatively well, and relates to the near infrared ray absorption methacrylic system resin Plastic solid which is fabricated the shape of a new methacrylic system resin constituent and a sheet, or a film excellent in near infrared ray absorbing power, and changes. Researches and developments are the functional material currently performed briskly, and especially the charge of a near infrared ray absorber can be used recently as optical materials, such as information record ingredients, such as sensitive material which makes the light source semiconductor laser light which has the wavelength of a near infrared region, and a record ingredient for optical disks, an infrared cut filter, and a film, and a heat ray absorptivity grading ingredient.

[0002]

[Description of the Prior Art] It is tungsten hexachloride as conventionally shown in U.S. Pat. No. 3692688 as a light transmission nature ingredient of near infrared ray absorptivity. (WCl₆) Tin chloride (SnCl₂·2H₂O) The ingredient excellent in the near infrared ray absorbing power which dissolves in methyl-methacrylate syrup (monomer) and is acquired by carrying out a polymerization and which does not have Hayes substantially is known. Furthermore, in addition to this as a charge of a near infrared ray absorber developed until now, it is [JP,61-218551,A / an anthraquinone derivative and] in a thiol nickel complex and JP,61-115958,A to chromium, cobalt complex salt, and JP,60-21294,B in JP,60-42269,B. 700-800nm The new squarylium compound which has absorption maximum wavelength in a field is indicated.

[0003]

[Problem(s) to be Solved by the Invention] although the conventional charge of a near infrared ray absorber had the trouble that as for the thing of an organic system endurance be bad and early capacity deteriorated in connection with change and the passage of time of an environmental condition and the thing of a complex system be durable on the other hand , not only the near-infrared section but the visible region had absorption , and there be a problem that there be much what the compound itself be color reinforcement , and an application will be restrict . Furthermore, on the wavelength as which the absorption peak was regarded in specific wavelength and both of the things of a system shifted [wavelength] from the peak, it was what absorbing power does not almost have. If the record object which makes the light source laser light which has the wavelength of the near-infrared section is considered using these materials, it is necessary to double the wavelength of a laser line, and the absorption peak of an ingredient. However, the combination with which also in the wavelength of a laser line the wavelength of a laser line and the absorption peak of the charge of a near infrared ray absorber agree since only that to which the absorption wavelength of the charge of a near-infrared absorber was also restricted is obtained could not but become a ***** thing.

[0004] Moreover, WCl₆ of the above-mentioned conventional technique The constituent which dissolved SnCl₂·2H₂O in methyl-methacrylate syrup colored in dark blue, and although it had the property which absorbs a near infrared ray well, it had the trouble of carrying out tenebrescence between prolonged neglect in a dark place. Thus, the photochromism which advances gently was a trouble which is not desirable when offering the industrial products equipped with fixed quality, such as a light filter and heat ray absorptivity grading.

[0005]

[Means for Solving the Problem] It comes to complete a header and this invention for the outstanding charge of a near infrared ray absorber made into the purpose being obtained by seeing absorption uniformly in this invention and the

800-2000nm whole near infrared region, and making a copper compound, a thiourea system derivative, or (reaching) a thioamide system derivative contain in methacrylic system resin, as a result of coloring repeating examination wholeheartedly about the charge of a near infrared ray absorber in which endurance was excellent few.

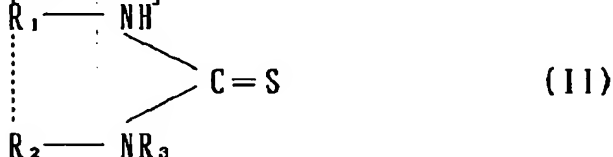
[0006] That is, this invention is (A). Methacrylic system resin It is (B) to the 100 weight sections. The following general formula (I)

(R-X)_nCu (I)

The inside of [type and R Hydrogen, an alkyl group, a cycloalkyl radical, an aryl group, The monad chosen from the group which consists of an aralkyl radical and heterocycle residue (each radical may have one or more substituents), The copper compound by which -COO, -SO₄, -SO₃, -PO₄, -O, and n are expressed with integer] of 1-4 for X, At least a kind of copper compound 0.05 chosen from chlorophyll copper, sodium copper-chlorophyllin, and bisacetylacetonate copper - 5 weight sections, and (C) The following general formula (II)

[0007]:

[Formula 3]



[0008] (R₁, R₂, and R₃ may express the monad chosen from the group which consists of the heterocycle residue of hydrogen, an alkyl group, a cycloalkyl radical, an aryl group, an aralkyl radical and 5 members, or 6 members, each radical may have one or more substituents, R₁, R₂, or R₂ and R₃ may connect, and they may form a ring) The thiourea derivative shown and the following general formula (III) [0009]

[Formula 4]



[0010] R₄ and R₅ -- hydrogen, an alkyl group, an alkenyl radical, and a cycloalkyl radical -- The monad chosen from the group which consists of the heterocycle residue of an aryl group, an aralkyl radical and 5 members, or 6 members is expressed. R₅ may also express an alkoxy group further and each radical may have one or more substituents. R₄ and R₅ may connect and they may form a ring. It is related with the near infrared ray absorption methacrylic system resin constituent characterized by the thing which is chosen from the thioamide derivative shown, and which contain at least one sort of 0.05 - 50 weight sections, and changes. Moreover, it is related with the near infrared ray absorption methacrylic system resin Plastic solid which the near infrared ray absorption methacrylic system resin constituent which consists of the aforementioned presentation is fabricated a sheet or in the shape of a film, and changes.

[0011] As a polymerization nature raw material used in manufacture of the resin ingredient of this invention, it is the polymerization nature partial saturation monomer which uses a methyl methacrylate or a methyl methacrylate as a principal component. As an example of a methyl methacrylate and the polymerization nature partial saturation monomer which can be copolymerized, it is an acrylic acid (meta) (semantics of an acrylic acid or a methacrylic acid.). Like the following, a methyl acrylate, an ethyl acrylate (meta), acrylic-acid (meta) propyl, Butyl acrylate, acrylic-acid (meta).cyclohexyl, 2-ethylhexyl acrylate (meta), (Meta) Ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, Tetra-ethylene GURIKORUJI (meta) acrylate, trimethylolethane tri(metha)acrylate, TORIMECHI roll pro pantry (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, neopentyl GURIKORUJI (meta) acrylate, an acrylic-acid (meta) allyl compound, acrylic-acid (meta) hydroxyethyl, etc. can mention as an example. When using the polymerization nature partial saturation monomer which uses a methyl methacrylate as a principal component as a polymerization raw material in this invention, it is desirable to include a methyl methacrylate 60% of the weight or more preferably 50% of the weight or more. It is desirable for the method of obtaining a partial polymerization object by massive precuring or the approach of dissolving a polymerization object in a monomer to be mentioned as an approach of obtaining the syrup which contains the polymer of this monomer in the polymerization

nature partial saturation monomer which uses a methyl methacrylate or a methyl methacrylate as a principal component as a polymerization raw material, as usually carried out, and to adjust to 35 or less % of the weight of polymer content in consideration of impregnation. Moreover, the suspension polymerization which are the following typical polymerization methods, an emulsion polymerization, and solution polymerization can also be used. Moreover, in case the methacrylic resin ingredient of this invention is manufactured by the polymerization, the radical polymerization initiator of an azo compound or organic peroxide is used as a polymerization initiator.

[0012] Moreover, although the following can be illustrated as a copper compound shown by the above-mentioned general formula (I) used by this invention, it is not limited to these. Stearin acid copper, PANAMICHIN ****, copper oleate, behenic acid copper, lauryl ****, Capric-acid copper, caproic-acid copper, valeric-acid copper, isobutyric-acid copper, butanoic acid copper, propionic-acid copper, Copper acetate, formic-acid copper, copper hydroxide, benzoic-acid copper, alt.toluic-acid copper, meta-toluic-acid copper, Para toluic-acid copper, PARATASHA rib chill benzoic-acid copper, alt.KURORU benzoic-acid copper, Dichloro benzoic-acid copper, Tori Krol benzoic-acid copper, p-bromine benzoic-acid copper, p-iodine benzoic-acid copper, o-benzoylbenzoic acid copper, p-nitrobenzoic acid copper, Anthranilic-acid copper, p-aminobenzoic acid copper, oxalic acid copper, malonic-acid copper, Succinic-acid copper, glutaric-acid copper, adipic-acid copper, pimelic-acid copper, suberic-acid copper, Azelaic-acid copper, sebacic-acid copper, phthalic-acid copper, monoester phthalic-acid copper, Copper naphthenate, naphthalene carboxylic-acid copper, tartaric-acid copper, diphenylamine-2-carboxylic-acid copper, 4-cyclohexyl butanoic acid copper, diethyldithiocarbamic acid copper, cupric gluconate, Diethoxy copper, G i-propoxy copper, octylic acid copper, alkylbenzene-sulfonic-acid copper, P-toluenesulfonic-acid copper, naphthalenesulfonic acid copper, naphthylaminesulfonic acid copper, n-dodecylbenzenesulfonic acid copper, a dodecyl copper sulfate, 2, 5-dimethylbenzene sulfonic-acid copper, 2-KARUBO methoxy-5-methylbenzene sulfonic-acid copper, alpha-naphthyl phosphoric-acid copper, G 2-ethylhexyl phosphoric-acid copper, isodecyl phosphoric-acid copper.

[0013] Although the following can be illustrated as a thiourea derivative shown by the general formula (II) used by this invention, it is not limited to these.

1-ethyl-3-phenyl thiourea, 1, 3-diphenyl thiourea, 1, 3-diethyl thiourea, 1-ethyl-3-p-chlorophenyl thiourea, 1-ethyl-3-(2-hydroxyethyl) thiourea, 1-(2-thiazolyl)-3-phenyl thiourea, 1 and 3-distearyl thiourea, 1, 3-dibehenyl thiourea, 1-ethyl thiourea, 1-p-BUROMO phenyl-3-phenyl thiourea, 1-(2-thiophenyl)-3-phenyl thiourea, 1, 3-screw (2-hydroxyethyl) thiourea, 1-p-aminophenyl-3-phenyl thiourea, 1-p-nitrophenyl-3-phenyl thiourea, 1-p-hydroxyphenyl-3-phenyl thiourea, 1, 3-G m-KURORU phenyl thiourea, Ethylene thiourea, thiourea, 1-methyl-3-p-hydroxyphenyl thiourea, 1-phenyl thiourea, 1-m-nitrophenyl thiourea, 1-p-nitrophenyl thiourea, 1-p-aminophenyl thiourea, 1, 3-dimethyl thiourea, 1, 3-dicyclohexyl thiourea, 1-phenyl-3-p-chlorophenyl thiourea, 1-phenyl-3-p-methoxyphenyl thiourea, 1, and 1-diphenyl thiourea, 1, and 1-dibenzyl-3-phenethyl thiourea, 1-phenyl-3-(2-hydroxyethyl) thiourea.

[0014] Although the following can be illustrated as a thioamide derivative shown by the general formula (III) used by this invention, it is not limited to these.

N-methylthio Benz amide, N-phenylthio Benz amide, N-ethyl thio ethyl amide, An N-ethyl thio-p-KURORU Benz amide, N-propyl thio Benz amide, N-ethyl thio stearyl amide, an N-1-(2-thiazolyl) thio Benz amide, N-stearyl thio stearyl amide, N-behenyl thio behenyl amide, Thioacetamide, an N-phenyl-thio-p-BUROMO Benz amide, An N-1-(2-thiophenyl) thio Benz amide, N-behenyl thioacetamide, An N-p-amino phenylthio Benz amide, an N-p-nitro phenylthio Benz amide, An N-p-hydroxy phenylthio Benz amide, an N-m-KURORU phenylthio Benz amide, Thio nicotinamide, a thio acetanilide, O-ethyl-N-phenyl (thio carbamate), A thio Benz amide, a thio-m-nitro Benz amide, thio-p-nitro Benz ANIDO, A thio-p-amino Benz amide, N-methylthio acetamide, N-cyclohexyl Benz amide, N-chloro phenylthio Benz amide, a N-p-methoxy phenylthio Benz amide, N-stearyl thio Benz amide.

[0015] The copper compound, thiourea derivative, or (reaching) thioamide derivative used in this invention can change visible and the amount made to contain by setup of the permeability of a near-infrared region. the addition of a copper compound -- methacrylic system resin the 100 weight sections -- receiving -- 0.05 - 5 weight section -- it is the 0.05 - 2.5 weight section preferably. moreover, the addition of a thiourea derivative -- methacrylic system resin the 100 weight sections -- receiving -- 0.05 - 50 weight section -- it is 0.05 - 10 weight section preferably. moreover, the addition of a thioamide derivative -- methacrylic system resin the 100 weight sections -- receiving -- 0.05 - 50 weight section -- it is 0.05 - 10 weight section preferably. Moreover, since it changes with the board thickness when the resin ingredient with which permeability is obtained at this invention is a plate also in the same content, it is necessary to determine a content as the appearance from which the permeability in the board thickness finally set up is obtained.

[0016] It sets to this invention and the addition of a copper compound, a thiourea derivative, or (reaching) a thioamide derivative is methacrylic system resin. As opposed to the 100 weight sections, respectively to the case of under the 0.05 weight section Improvement in near infrared ray absorbing power is not enough, and, on the other hand, the addition of a copper compound is methacrylic system resin 100. In exceeding 5 weight sections to the weight section For the improvement in near infrared ray absorbing power, it does not see and the addition of a thiourea derivative or (reaching) a thioamide derivative is methacrylic system resin. In exceeding 50 weight sections to the 100 weight sections, improvement in near infrared ray absorbing power is not found, but there is a possibility that Hayes may occur in an ingredient.

[0017] In addition, besides the above-mentioned component, reinforcing materials, such as the additive currently generally used if needed, for example, a flame retarder, a thermostabilizer, an anti-oxidant, light stabilizer, an ultraviolet ray absorbent, lubricant, a coloring agent, an inorganic bulking agent, and a glass fiber, etc. can also be blended. It can manufacture easily with general-purpose mixed equipment, for example, a hot calender roll, a Banbury mixer, or an extruder, without requiring a special means and a mixed sequence foreword as the mixed approach of the methacrylic system resin in this invention, a thiourea derivative, a thioamide derivative, and a copper compound. A film or a sheet is easy to be manufactured according to the usual manufacturing method. It can manufacture by the T-die method by the extruder, the inflation-molding method, the calender fabricating method, and compression forming. Although there is nothing, since especially a limit is within the limits of 0.01-10mm, its thickness of a film or a sheet is desirable. In addition, when increasing the reinforcement of a sheet further or attaching a pattern, the interior is made to contain the glass fiber network and the wire gauze made from stainless steel which knit and wove glass filament yarn in the shape of [of about 5mm angle] a grid, and they may be fabricated.

[0018]

[Function] carrying out heating kneading of the mixture which contained the copper compound of a general formula (I) or chlorophyll copper, sodium copper-chlorophyllin, bisacetylacetone copper, the thiourea derivative of a general formula (II), or the thioamide derivative of a general formula (III) like the above by the above-mentioned mixed approach at methacrylic system resin -- the 800-2000nm whole region -- crossing -- about -- it comes to absorb a near infrared ray to Mr. one. So that clearly from the example and the example of a comparison which are shown below, although the reason is not clear Even if it carries out heating kneading of a thiourea derivative, a thioamide derivative, or the copper compound independently at methacrylic system resin, respectively And a near infrared ray is not absorbed strongly. the 800-2000nm near infrared region whole region -- crossing -- about -- Mr. one -- If it carries out from the same being said of having mixed methacrylic system resin, the thiourea derivative or the thioamide derivative, and the copper compound By carrying out heating kneading by the above-mentioned mixed approach, the mixture containing a thiourea derivative or a thioamide derivative, and a copper compound to methacrylic system resin A certain reaction occurs between a thiourea derivative or a thioamide derivative, and a copper compound, and it is presumed that it is because complex (complex) is generated.

[0019]

[Example] Hereafter, although detail of this invention is given according to an example, this invention is not restricted to these examples. All the addition rates in an example and the example of a comparison show the weight section. Moreover, the transparency spectrum of the obtained resin ingredient is a spectrophotometer (Hitachi Make: 323 molds). It measured. the judgment of near infrared ray absorptivity -- the average of 900, 1000, and an absorption value with a wavelength [each] of 1100 or 1500nm made O and 30% or more **, and made [80% or more of thing] 30% or less x for O and 60% or more.

[0020] The heat of near infrared ray absorptivity, humidity, and the stability over light were measured by the following approach.

Thermal resistance and moisture resistance: It is a spectrophotometer again about the near infrared ray absorptivity after leaving a near infrared ray absorptivity sheet in the oven of 80 degrees C and 100%RH for 480 hours. (1000nm) It measured. The result computed by the following type estimated the shelf life.

[0021]

[Equation 1]

$$\text{保存率} = \frac{100 - \text{加熱・加湿後の透過率}}{100 - \text{加熱・加湿前の透過率}} \times 100(\%)$$

[0022] Lightfastness: Be about a near infrared ray absorptivity sheet with UV (ultraviolet rays) circuit tester (super-[made from Great Japan Plastics] promotion fading-test machine). It is a spectrophotometer again about the near infrared ray absorptivity after carrying out an optical exposure for 200 hours. (1000nm) It measured. The result computed by the following type estimated the shelf life.

[0023]

[Equation 2]

$$\text{保存率} = \frac{100 - \text{露光後の透過率}}{100 - \text{露光前の透過率}} \times 100(\%)$$

[0024] An injection molding machine is used for thermal stability. It fabricated with the laying temperature of 230 degrees C after [of the residence time] 20 minutes, color tone change of the obtained sample was measured with the color difference meter by Nippon Denshoku Co., Ltd., the color difference (deltaE) was searched for by the L.a.b. method, and it judged as follows.

O :superior O:fitness ** : nothing [YAKE] (yellow change size)

x: The thiourea compound 2 weight section and the copper compound of combination which are shown in one to YAKE owner example 23 table 1, and Table 2 It is methacrylic resin about the 0.2 weight sections. It adds in the 100 weight sections, mixes for 20 minutes by the tumbler mixer, and is 40mmphi extrusion briquetting machine. It was made the pellet after kneading at 220 degrees C. Subsequently, this pellet was dried and the green transparence resin plate which does not have Hayes with a thickness of 3mm using an injection molding machine was produced. The transparency spectrum was measured about these obtained plates. Although the result was shown in Table 4, it excelled in the absorptivity of a near-infrared region.

[0025] It is methacrylic resin about a thiourea compound and a copper compound at the combination and the addition which are shown in 24 to example 33 table 2. It adds in the 100 weight sections, mixes for 20 minutes by the tumbler mixer, and is 40mmphi extrusion briquetting machine. It was made the pellet after kneading at 220 degrees C. Subsequently, this pellet was dried and the green transparence resin plate which does not have Hayes with a thickness of 3mm using an injection molding machine was produced. The transparency spectrum was measured about these obtained plates. Although the result was shown in Table 5, it excelled in the absorptivity of a near-infrared region.

[0026] They are the thioamide compound 2 weight section and a copper compound in the combination shown in 34 to example 37 table 2. It is methacrylic resin about the 0.2 weight sections. It adds in the 100 weight sections, mixes for 20 minutes by the tumbler mixer, and is 40mmphi extrusion briquetting machine. It was made the pellet after kneading at 220 degrees C. Subsequently, this pellet was dried and the green transparence resin plate which does not have Hayes with a thickness of 3mm using an injection molding machine was produced. The transparency spectrum was measured about these obtained plates. Although the result was shown in Table 5, it excelled in the absorptivity of a near-infrared region.

[0027]

[Table 1]

熱可塑性樹脂の配合処方

実施例 No.	配 合 処 方 (重量部)			メタクリル系樹脂
	チオ尿素化合物	銅化合物		
1	1,3-ジフェニルチオ尿素	2	p-クロル安息香酸銅	PMMA 100
2	1,3-ジラウリルチオ尿素	2	"	PMMA 100
3	1,3-ジエチルチオ尿素	2	"	PMMA 100
4	1,3-ジメチルチオ尿素	2	"	PMMA 100
5	1,3-ジ-m-クロルフェニルチオ尿素	2	"	PMMA 100
6	1,3-ジフェニルチオ尿素	2	ステアリン酸銅	PMMA 100
7	"	2	ベヘン酸銅	PMMA 100
8	"	2	p-ニトロ安息香酸銅	PMMA 100
9	1,3-ジフェニルチオ尿素+1,3-ジクロルフェニルチオ尿素(1:1)	2	m-クロル安息香酸銅	PMMA 100
10	1,3-ジフェニルチオ尿素	2	p-ブロム安息香酸銅	PMMA 100
11	"	2	安息香酸銅	PMMA 100
12	"	2	o-ベンゾイル安息香酸銅	PMMA 100
13	"	2	銅クロロフィル	PMMA 100
14	"	2	グルコン酸銅	PMMA 100
15	"	2	4-シクロロヘキシル酪酸銅	PMMA 100

[0028]
[Table 2]

熱可塑性樹脂の配合処方

実施例 No.	配 合 処 方 (重量部)			メタクリル系樹脂
	チオ尿素化合物/チオアミド化合物	銅 化 合 物		
16	1,3-ジフェニルチオ尿素	n-ドデシルベンゼンスルホン酸銅	2	PMMA 100
17	"	ナフタリンスルホン酸銅	2	PMMA 100
18	"	α -ナフチルリン酸銅	2	PMMA 100
19	"	ステアリン酸銅+n-クロル安息香酸銅(1:1)	2	PMMA 100
20	"	ステアリン酸銅	2	PMMA 100
21	"	酢 酸 銅	2	PMMA 100
22	"	コハク酸銅	2	PMMA 100
23	"	グルタル酸銅	2	PMMA 100
24	"	p-クロル安息香酸銅	2	PMMA 100
25	"	"	4	PMMA 100
26	"	"	1	PMMA 100
27	"	"	2	PMMA 100
28	1,3-ジ-n-クロルフェニルチオ尿素	"	2	PMMA 100
29	"	"	4	PMMA 100
30	"	"	1	PMMA 100
31	"	"	2	PMMA 100
32	1,3-ジラウリルチオ尿素	"	2	PMMA 100
33	"	"	2	PMMA 100
34	N-フェニルチオベンツアミド	"	2	PMMA 100
35	N-シクロヘキシルチオベンツアミド	"	2	PMMA 100
36	N-ステアリルチオベンツアミド	"	2	PMMA 100
37	チオアセトアニリド	"	2	PMMA 100

[0029] Combination of the combination of example 38 example 1 is mixed for 20 minutes by the tumbler mixer, and it is 40mmphi extruding press machine. It sheet-sized to 1mm thickness by the T-die fabricating method at 220 degrees C. The temperature of a cooling roller was 95 degrees C. Although this resin sheet comparatively often penetrated the light of a visible region so that the comparison with the transparency spectrum B of the usual methacrylic resin sheet which does not contain the near infrared ray absorbent shown in this drawing might show, although A in drawing 1 shows the transparency spectrum of the obtained transparency resin sheet, it excelled in the absorptivity of the near-infrared region which is not looked at by the usual methacrylic resin sheet.

[0030] It is methacrylic resin at independent respectively about the thiourea compound, thioamide compound, or

copper compound shown in one to example of comparison 9 table 3. It adds in the 100 weight sections, mixes for 20 minutes by the tumbler mixer, and is 40mmphi extrusion briquetting machine. It was made the pellet after kneading at 220 degrees C. Subsequently, this pellet was dried and the green transparence resin plate which does not have Hayes with a thickness of 3mm using an injection molding machine was produced. The transparency spectrum was measured about these obtained plates. Although the result was shown in Table 5, there was only 30% or less of near infrared ray absorptivity altogether.

[0031]

[Table 3]

比較例 No.	配 合 処 方 (重量部)		
	チオ尿素化合物/チオアミド化合物	銅 化 合 物	メタクリル系樹脂
1	—	—	PMMA 100
2	1,3-ジフェニルチオ尿素	—	PMMA 100
3	1,3-ジラウリルチオ尿素	—	PMMA 100
4	1,3- <i>m</i> -クロルフェニルチオ尿素	—	PMMA 100
5	N-フェニルチオベンツアミド	〃	PMMA 100
6	N-シクロヘキシルチオベンツアミド	〃	PMMA 100
7	—	p-クロル安息香酸銅	PMMA 100
8	—	ペヘン酸銅	PMMA 100
9	—	ステアリン酸銅	PMMA 100

[0032] .
[Table 4]

近赤外線吸収性樹脂の評価結果

	単 位	実 施 例																			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
近赤外線吸収性	—	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎
耐熱性、耐湿性	%	99	97	95	96	94	94	96	97	96	96	97	96	97	95	96	98	95	95	96	93
耐 光 性	%	98	96	95	92	94	95	96	96	95	92	96	94	91	90	92	95	95	93	95	92
熱安定性	230℃×20分 ΔE	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○

[0033]
[Table 5]

近赤外線吸収性樹脂の評価結果

	单 位	实 施 例												比 較 例										
		24	25	26	27	28	29	30	31	32	33	34	35	36	37	1	2	3	4	5	6	7	8	9
近赤外線吸収性	—	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	×	×	×	×	×	×	×	×	×
耐熱性、耐湿性	%	96	97	95	96	94	95	96	96	97	95	97	97	94	92	—	—	—	—	—	—	—	—	—
耐 光 性	%	97	96	94	94	93	91	97	97	96	94	96	95	93	92	—	—	—	—	—	—	—	—	—
熱安定性	230℃×20分 ΔE	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○

[0034] It is clear the sheet's of the methacrylic system resin which kneaded the thiourea compound or the thioamide compound, and the copper compound according to Table 4 and Table 5 to become a strong near infrared ray absorptivity sheet. Moreover, this near infrared ray absorptivity hardly falls by heating, humidification, or exposure, but it turns out to change of the environmental condition of handling or preservation that it is extremely stable. The sheet of the methacrylic system resin which kneaded independently the thiourea compound, the thioamide compound, or the copper compound did not show near infrared ray absorptivity substantially.

[0035]

[Effect of the Invention] Since the photochromism of carrying out tenebrescence is not seen, either, even if there is no instability, such as tenebrescence, and it leaves it in a dark place for a long period of time, but the resin ingredient which carries out heating kneading of the near infrared ray absorption methacrylic system resin constituent of this invention, is fabricated a sheet or in the shape of a film, and changes shows the outstanding near infrared ray absorptivity, it is industrially useful as optical filter and heat ray absorptivity grading material etc. Moreover, obtained near infrared ray absorption sheet It has the strong absorptivity across which it goes throughout a 800-2000nm near infrared region. It can use by using these properties as optical materials, such as a near infrared ray cut-off filter, a record ingredient, a heat ray shielding material, an accumulation ingredient, a near infrared ray detection sensor, etc. Although the constituent of this invention contains the metal, since there is little coloring, the Plastic solid of the sheet containing these, a film, etc. becomes the thing excellent in the appearance.

[Translation done.]